

Synthesis, Characterization of Organotin(IV) Complexes of Schiff Base Ligands and Evaluation of Their Biological Activities Against Pathogenic Bacteria and Fungi

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Abstract

Organotin complexes show wide analytical applications as antioxidant, anti-inflammatory, anti-tumor, antileishmanial. There this study focuses on synthesis and characterization of Organotin(IV) complexes with Schiff base ligands with potent biological activities. In this study attention is given on the synthesis and characterization of diorganotin complexes of Schiff bases of 1,3-diketones along with the biological applications as antibacterial against gram +ve, gram -ve, and antifungal against pathogenic fungi. The synthesized complexes were prepared by reaction of β -diketones and aminophenols. NMR studies, IR studies, mass analysis, determined the characterized complexes. All the complexes showed biological potency. The phenyl complexes show more activity.

Introduction

Organotin(IV) compounds have acknowledged marvelous awareness for their synthesis¹, characterization and biological activities. Moreover, Organotin compounds have capability to make stable bonds with carbon and heteroatoms² like nitrogen and oxygen that have established abundant awareness in intellectual and applied analysis.³ The design and synthesis of Schiff's bases synthesized from β -diketones and their organotin complexes having novel structural,⁴ delicate balance⁵ and noteworthy physico-chemical properties⁶ symbolize an active space of analysis in coordination chemistry and have important value in biological processes. Organotin compounds illustrate an outsized quantity of assorted succession of applications because of their chemical and biological necessities.⁷⁻⁸ Organotin(IV) compound's biological activity is greatly influenced by the coordination number⁹ of the tin atom and also the stereochemistry¹⁰ of the compound. Schiff bases still play an essential role in coordination chemistry an excellent extent of Schiff bases are widely synthesized because of various biomedical, commercial applications and medicative utilities.¹¹ Organotin complexes show wide analytical applications as antioxidant, anti-inflammatory, anti-tumor, antileishmanial¹²⁻¹³. The tin metal interaction to the Schiff base ligands via oxygen and nitrogen forming O-Sn and N-Sn bonds prompted a much interest in antibacterial and antifungal activities.¹⁴⁻¹⁵ Thus we focused on study of Organotin(IV) complexes with Schiff base ligands with potent biological activities. Herein, we are paying attention on the synthesis and characterization of diorganotin complexes of Schiff bases of 1,3-diketones along with the biological applications as antibacterial against gram +ve, gram -ve, and antifungal against pathogenic fungi.

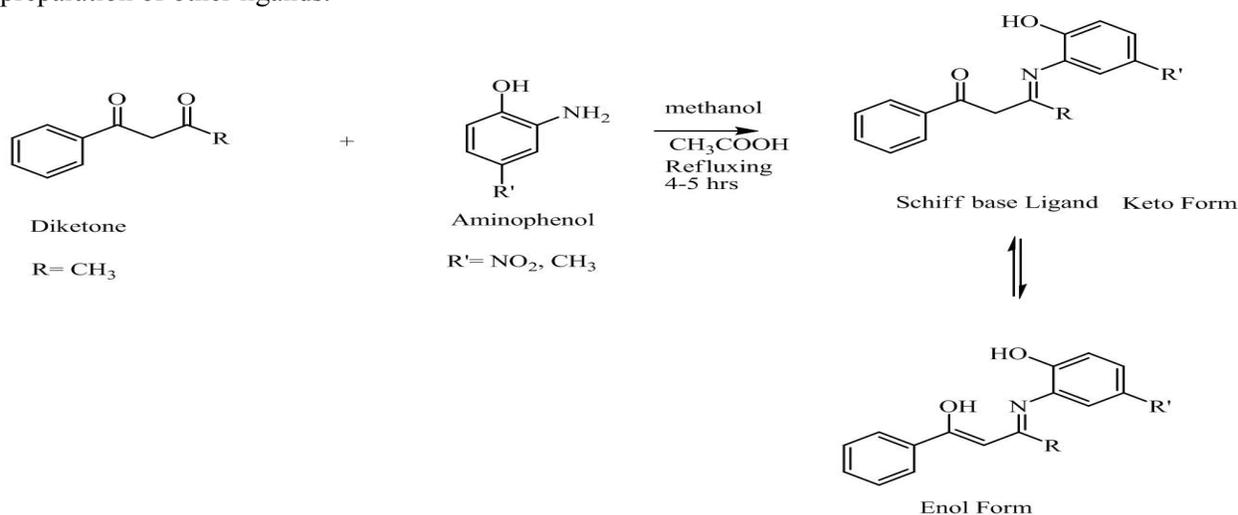
Material and Methods

All the chemicals (benzoyl acetone, 4-nitro-2-aminophenol, 4-methyl-2-aminophenol) were purchased from Aldrich and Himedia and were used as provided without any further purification. All the used reagents and solvents were dried, distilled and refined by their standard ways of purification and purity of

the compounds was checked frequently by thin layer chromatography (TLC). The reactions were carried out beneath anhydrous surroundings and therefore the Organotin(IV) complexes, chemicals and glass equipment have been placed within the surroundings free from moisture. Tin content was estimated gravimetrically as SnO₂. Elemental analysis (C, H, and N) were analyzed on Perkin-Elmer 2400 instrument (Waltham, Massachusetts) IR spectra were recorded on Shimadzu IR affinity-I 8000 FT-IR spectrometer using KBr pellets having wavelength vary 400-4000 cm⁻¹. NMR spectra were recorded in CDCl₃ and DMSO-*d*₆ on Bruker Avance II 400 MHz NMR spectroscope and TMS was used as internal standard all chemical shifts were considered in parts per million (ppm).

Synthesis of Schiff base ligands

The Schiff base ligands were prepared by condensation of β-diketone (benzoyl acetone) and aminophenol derivatives (2-aminophenol and 4-methyl-2-aminophenol). A methanolic solution of benzoyl acetone (5mmol) was added to methanolic solution of 4-methyl-2-aminophenol (5mmol) and 2-3 drops of acetic acid was added to the solution as catalyst. The solution was refluxed for about 5-6 hours and then the mixture obtained were kept overnight at room temperature. The product was filtered, recrystallised from methanol. The solid obtained was collected and checked by TLC. A similar procedure was used for the preparation of other ligands.



Scheme 1: Route for the synthesis of Schiff base ligands

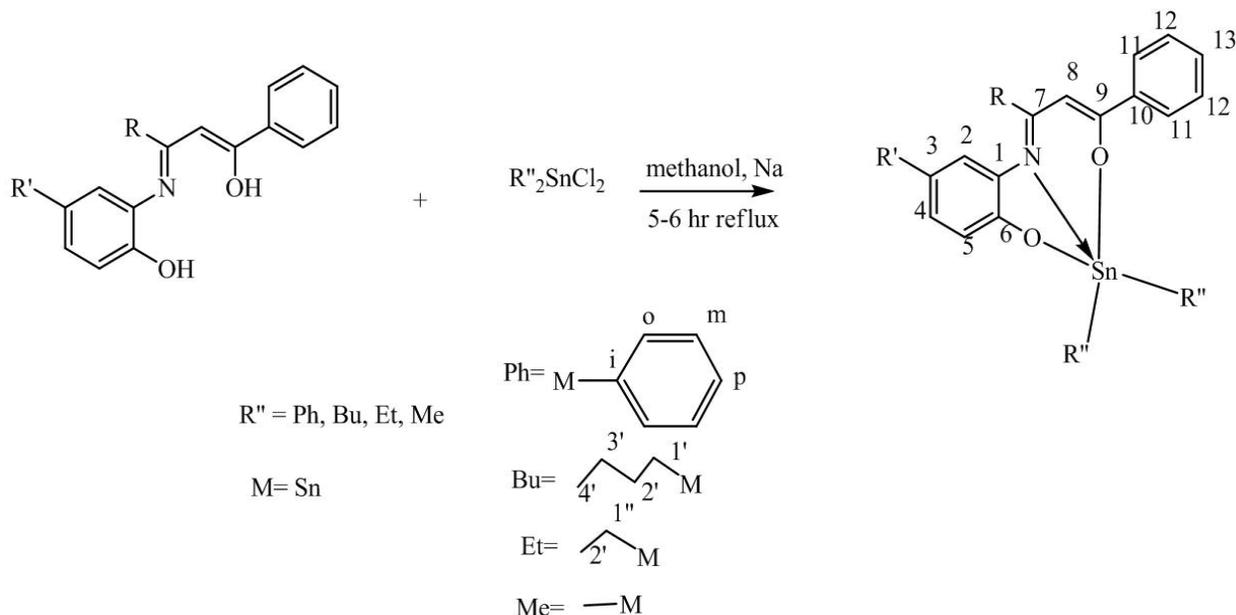
Synthesis of Organotin (IV) complexes

A small piece of sodium was added to the methanol and then the ligand was added to the solution. The solution was refluxed for about 2h to get the sodium salt of Schiff base. After that, the methanolic solution of diorganotin dichloride was added to reaction mixture and refluxed for about 5-6 hr. The sticky compound was obtained, and stickiness was removed by dry hexane. The solid was collected and dried over vacuum. The same method was adopted for the preparation of the other complexes.

Synthesis of ligand H₂L₁ [2-((E)-((Z)-4-hydroxy-4-phenylbut-3-en-2-ylidene)amino)-4-methylphenol]

Yield: 82%. IR (KBr) ν 3200 (O-H), 1601 (C=N), cm⁻¹. ¹H NMR (CDCl₃) δ 1.58 (s, 3H, CH₃), 2.23 (s, 3H, CH₃), 5.63 (s, 1H, H-8), 6.80 (s, 1H, H-2), 6.91-6.98 (m, 2H, ArH), 7.40-7.46 (m, 3H, ArH), 7.85-7.87 (m, 2H, ArH), 9.02 (s, 1H, D₂O-exchangeable, OH), 12.33 (s, 1H, D₂O-exchangeable, OH). ¹³C

NMR (CDCl₃) δ 19.69 (CH₃), 20.42 (CH₃), 94.31 (C-8), 117.10, 124.69, 127.30, 127.88, 128.24, 129.21, 130.86, 139.91 (ArC), 150.08 (C-9), 165.58(C-7), 188.17 (C-6). Anal. Calcd. for C₁₇H₁₇NO₂: (Mol. Wt. 267.32), (C, 76.38; H, 6.41; O, 5.24; N, 11.97). Found: (C, 76.34; H, 6.43; O, 5.22; N, 11.99).



Scheme 2: Route for the synthesis of Organotin complexes

Synthesis of ligand H₂L₂ [2-((E)-((Z)-4-hydroxy-4-phenylbut-3-en-2-ylidene)amino)-4-nitrophenol]

Yield: 86%. IR (KBr) ν 3372 (O-H), 1607 (C=N) cm⁻¹. ¹H NMR (CDCl₃) δ 2.29 (s, 3H, CH₃), 5.67 (s, 1H, H-8), 6.82 (s, 1H, H-2), 6.89-6.91 (m, 2H, ArH), 7.38-7.42 (m, 3H, ArH), 7.89-7.91 (m, 2H, ArH), 9.06 (s, 1H, D₂O-exchangeable, OH), 12.36 (s, 1H, D₂O-exchangeable, OH). ¹³C NMR (CDCl₃) δ 20.18 (CH₃), 94.04 (C-8), 116.82, 124.43, 127.03, 127.62, 127.98, 129.95, 130.60, 139.64 (ArC), 149.82 (C-9), 165.32 (C-7), 187.90 (C-6). Anal. Calcd. for C₁₆H₁₄N₂O₄: (Mol. Wt. 298.10), (C, 64.42; H, 4.73; O, 21.45; N, 9.39). Found: (C, 64.12; H, 4.56; O, 21.14; N, 9.09).

Synthesis of complex Ph₂SnL₁ [(4Z,6E)-6,9-dimethyl-2,2,4-triphenylbenzo [d][1,3,6,2] dioxazastannone]

Yield: 72%. IR (KBr) ν 1587 (C=N), 436 (Sn-N), 559 (Sn-O), 691 (Sn-C) cm⁻¹. ¹H NMR (DMSO-d₆) δ 1.56 (s, 3H, CH₃), 2.26 (s, 3H, CH₃), 6.03 (s, 1H, H-8), 6.99 (s, 1H, H-2), 7.34-7.40 (m, 10H, Ph), 7.50-7.53 (m, 2H, ArH), 7.86-7.89 (m, 2H, ArH), 8.01-8.03 (m, 2H, ArH). ¹³C NMR (DMSO-d₆) δ 19.89 (CH₃), 20.95 (CH₃) 98.46 (C-8), 117.41, 118.50, 127.18, 128.13, 128.61, 129.78, 130.22, 132.34, 135.11, 136.43, 138.79 (ArC), 155.83 (C-9), 172.83 (C-7), 178.73 (C-6). ¹¹⁹Sn NMR (DMSO-d₆) δ -322.43. Anal. Calcd. for C₂₉H₂₅NO₂Sn: (Mol. Wt. 538.22), (C, 64.71; H, 4.68; O, 2.60; N, 5.95; Sn, 22.06). Found: (C, 64.74; H, 4.64; O, 2.62; N, 5.94; Sn, 22.03).

Synthesis of complex Bu₂SnL₁ [(4Z,6E)-2,2-dibutyl-6,9-dimethyl-4-phenylbenzo[d][1,3,6,2] dioxazastannone]

Yield: 71%. IR (KBr) ν 1583 (C=N), 436 (Sn-N), 558 (Sn-O), 690 (Sn-C) cm⁻¹. ¹H NMR (DMSO-d₆) δ 0.71-0.75 (t, 6H, H-4'), 1.17-1.22 (m, 4H, H-3'), 1.56 (s, 3H, CH₃), 1.88-1.89 (m, 4H, H-2'), 1.91-1.92

(t, 4H, H-1'), 2.26 (s, 3H, CH₃) 6.03 (s, 1H, H-8), 6.99 (s, 1H, H-2), 7.50-7.53 (m, 2H, ArH), 7.86-7.89 (m, 3H, ArH), 7.88-7.90, (m, 2H, ArH). ¹³C NMR (DMSO-d₆) δ 13.74 (C-4'), 19.91 (CH₃), 20.43 (CH₃), 25.09 (C-3'), 35.04 (C-2'), 39.02 (C-1'), 98.29 (C-8), 117.81, 118.30, 127.15, 127.21, 128.19, 128.76, 129.76, 138.73 (ArC), 157.17 (C-9), 171.98 (C-7), 179.21 (C-6). ¹¹⁹Sn NMR (DMSO-d₆) δ -210.62. Anal. Calcd. for C₂₅H₃₃NO₂Sn: (Mol. Wt. 498.25), (C, 60.27; H, 6.68; O, 2.81; N, 6.42; Sn, 23.83). Found: (C, 60.25; H, 6.64; O, 2.84; N, 6.45; Sn, 23.84).

Synthesis of complex Et₂SnL₁[(4Z,6E)-2,2-diethyl-6,9-dimethyl-4-phenylbenzo[d][1,3,6,2]dioxazastannone]

Yield: 74%. IR (KBr) ν 1580 (C=N), 457 (Sn-N), 559 (Sn-O), 647 (Sn-C) cm⁻¹. ¹H NMR (DMSO-d₆) δ 0.98 (t, 6H, H-2''), 1.56 (s, 3H, CH₃), 1.67 (q, 4H, H-1''), 2.26 (s, 3H, CH₃), 6.05 (s, 1H, H-8), 6.97 (s, 1H, H-2), 7.49-7.52 (m, 2H, ArH), 7.84-7.87 (m, 3H, ArH), 7.97-7.99 (m, 2H, ArH). ¹³C NMR (DMSO-d₆) δ 9.05 (C-2''), 14.06 (C-1''), 19.84 (CH₃), 20.31 (CH₃), 99.10 (C-8), 117.79, 118.53, 127.28, 128.39, 128.72, 129.21, 132.35, 136.88 (ArC), 156.91 (C-9), 171.91 (C-7), 179.71 (C-6). ¹¹⁹Sn NMR (DMSO-d₆) δ -180.23. Anal. Calcd. for C₂₁H₂₅NO₂Sn: (Mol. Wt. 442.41), (C, 57.05; H, 5.70; O, 3.17; N, 7.24; Sn, 26.85). Found: (C, 56.98; H, 5.65; O, 3.12; N, 7.15; Sn, 26.89).

Synthesis of complex Me₂SnL₁[(4Z,6E)-2,2,6,9-tetramethyl-4-phenylbenzo[d][1,3,6,2]dioxazastannone]

Yield: 74%. IR (KBr) ν 1577 (C=N), 437 (Sn-N), 556 (Sn-O), 618 (Sn-C) cm⁻¹. ¹H NMR (DMSO-d₆) δ 0.86 (t, 6H, M-CH₃), 1.56 (s, 3H, CH₃), 2.26 (s, 3H, CH₃), 6.02 (s, 1H, H-8), 6.95 (s, 1H, H-2), 7.47-7.51 (m, 2H, ArH), 7.82-7.85 (m, 3H, ArH), 7.95-7.97 (m, 2H, ArH). ¹³C NMR (DMSO-d₆) δ 8.05 (M-CH₃), 19.90 (CH₃), 20.47 (CH₃), 99.15 (C-8), 117.71, 118.48, 127.18, 128.31, 128.67, 129.72, 132.39, 136.81 (ArC), 156.83 (C-9), 171.21 (C-7), 178.91 (C-6). ¹¹⁹Sn NMR (DMSO-d₆) δ -125.24. Anal. Calcd. for C₁₉H₂₁NO₂Sn: (Mol. Wt. 414.09), (C, 55.11; H, 5.11; O, 3.38; N, 7.73; Sn, 28.67). Found: (C, 55.01; H, 5.03; O, 3.34; N, 7.71; Sn, 28.63).

Synthesis of complex Ph₂SnL₂[(4Z,6E)-6-methyl-9-nitro-2,2,4-triphenylbenzo[d][1,3,6,2]dioxazastannone]

Yield: 72%. IR (KBr) ν 1599 (C=N), 448 (Sn-N), 554 (Sn-O), 698 (Sn-C) cm⁻¹. ¹H NMR (DMSO-d₆) δ 2.29 (s, 3H, CH₃), 6.08 (s, 1H, H-8), 6.98 (s, 1H, H-2), 7.32-7.38 (m, 10H, Ph), 7.57-7.59 (m, 2H, ArH), 7.89-7.91 (m, 3H, ArH), 8.12-8.14 (m, 2H, ArH). ¹³C NMR (DMSO-d₆) δ 20.21 (CH₃), 99.26 (C-8), 117.79, 118.53, 127.10, 128.58, 128.67, 129.79, 130.27, 132.39, 135.18, 136.40, 138.72 (ArC), 155.79 (C-9), 172.90 (C-7), 178.81 (C-6). ¹¹⁹Sn NMR (DMSO-d₆) δ -302.18. Anal. Calcd. for C₂₈H₂₄N₂O₄Sn: (Mol. Wt. 571.21), (C, 58.87; H, 4.23; O, 11.20; N, 4.90; Sn, 20.78). Found: (C, 58.65; H, 4.12; O, 11.02; N, 4.78; Sn, 20.65).

Synthesis of complex Bu₂SnL₂[(4Z,6E)-2,2-dibutyl-6-methyl-9-nitro-4-phenylbenzo[d][1,3,6,2]dioxazastannone]

Yield: 73%. IR (KBr) ν 1577 (C=N), 434 (Sn-N), 558 (Sn-O), 692 (Sn-C) cm⁻¹. ¹H NMR (DMSO-d₆) δ 0.72-0.76 (t, 6H, H-4'), 1.18-1.23 (m, 4H, H-3'), 1.69-1.71 (m, 4H, H-2'), 1.83-1.85 (m, 4H, H-1'), 2.29 (s, 3H, CH₃), 6.03 (s, 1H, H-8), 6.97 (s, 1H, H-2), 7.55-7.57 (m, 2H, ArH), 7.84-7.86 (m, 3H, ArH), 8.02-8.04 (m, 2H, ArH). ¹³C NMR (DMSO-d₆) δ 13.79 (C-4'), 20.22 (CH₃), 25.21 (C-3'), 35.13 (C-2'), 39.08 (C-1'), 99.29 (C-8), 117.85, 118.31, 127.18, 128.71, 129.72, 131.37, 132.39, 136.71 (ArC), 157.71 (C-9),

171.95 (C-7), 179.36 (C-6). ^{119}Sn NMR (DMSO- d_6) δ -205.12. Anal. Calcd. for $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_4\text{Sn}$: (Mol. Wt. 531.23), (C, 54.26; H, 6.07; O, 12.05; N, 5.27, Sn, 22.35). Found: (C, 54.02; H, 5.89; O, 11.86; N, 4.98; Sn, 22.21).

Synthesis of complex $\text{Et}_2\text{SnL}_2[(4Z,6E)\text{-}2,2\text{-diethyl-}6\text{-methyl-}9\text{-nitro-}4\text{-phenylbenzo[d][1,3,6,2]dioxazastannonine}]$

Yield: 76%. IR (KBr) ν 1594 (C=N), 452 (Sn-N), 558 (Sn-O), 650 (Sn-C) cm^{-1} . ^1H NMR (DMSO- d_6) δ 0.97 (t, 6H, H-2''), 1.65 (q, 4H, H-1''), 2.29 (s, 3H, CH_3), 6.03 (s, 1H, H-8), 6.98 (s, 1H, H-2), 7.55-7.57 (m, 2H, ArH), 7.85-7.89 (m, 3H, ArH), 8.07-8.09 (m, 2H, ArH). ^{13}C NMR (DMSO- d_6) δ 9.02 (C-2''), 14.62 (C-1''), 20.26 (CH_3), 99.18 (C-8), 117.71, 118.58, 127.22, 128.71, 129.28, 131.26, 132.32, 136.85 (ArC), 156.89 (C-9), 171.99(C-7), 179.91 (C-6). ^{119}Sn NMR (DMSO- d_6) δ -190.73. Anal. Calcd. for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4\text{Sn}$: (Mol. Wt. 475.13), (C, 50.56; H, 5.09; O, 13.47; N, 5.90; Sn, 24.98). Found: (C, 50.43; H, 4.86; O, 13.27; N, 5.78; Sn, 24.79).

Synthesis of complex $\text{Me}_2\text{SnL}_2[(4Z,6E)\text{-}2,2,6\text{-trimethyl-}9\text{-nitro-}4\text{-phenylbenzo[d][1,3,6,2]dioxazastannonine}]$

Yield: 73%. IR (KBr) ν 1591 (C=N), 438 (Sn-N), 557 (Sn-O), 626 (Sn-C) cm^{-1} . ^1H NMR (DMSO- d_6) δ 0.91 (t, 6H, M- CH_3), 2.29 (s, 3H, CH_3), 6.04 (s, 1H, H-8), 6.98 (s, 1H, H-2), 7.52-7.55 (m, 2H, ArH), 7.86-7.89 (m, 3H, ArH), 8.01-8.03 (m, 2H, ArH). ^{13}C NMR (DMSO- d_6) δ 8.15 (M- CH_3), 20.20 (CH_3), 99.39 (C-8), 117.74, 118.47, 127.21, 128.68, 129.74, 131.39, 132.41, 136.89 (ArC), 156.73 (C-9), 172.91 (C-7), 178.99 (C-6). ^{119}Sn NMR (DMSO- d_6) δ -166.72. Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4\text{Sn}$: (Mol. Wt. 447.07), (C, 48.36; H, 4.51; O, 14.31; N, 6.27; Sn, 26.55). Found: (C, 48.14; H, 4.24; O, 14.10; N, 6.01; Sn, 26.43).

Results & Discussion

General

The reaction was carried out in 1:1 molar ratio in methanol as solvent. Schiff base ligands H_2L reacted with Organotin compound dialkyltin dichloride R_2SnCl_2 in 1:1 molar ratio in super dried methanol. 1:1 condensation occurred only even we use excess of amine. Most of the Organotin complexes were obtained as sticky products; the stickiness was removed by dry hexane. The solid thus obtained was dried over vacuum. All the complexes were found to be soluble in CDCl_3 and DMSO.

Electronic Spectra (UV-Visible Spectra)

In the electronic spectra of ligands, a band appearing at 220 nm is assigned for phenyl ring that shifted to higher wavelength 245-258 nm in complexes. An azomethine group appeared at 295 nm that also get shifted to higher wavelength in complexes. The electronic spectra of prepared ligands and their corresponding complexes were recorded in methanol solution. They exhibited bands around 290 nm and 410 nm due to π - π^* and n - π^* transitions within the azomethine cluster. The primary band remained without change within the complexes, whereas the other get shifted to lower wavelength in complexes as a result of coordination of nitrogen to the central metal atom. The ligand shows four bands at 340, 320, 280 and 240 nm which can ensue to n - π^* and π - π^* transitions. All the complexes showed bands within the 350-300 and 300-240 nm ranges which assigned to intra-ligand transitions.¹⁶⁻¹⁷

IR Spectra

On comparison of infrared spectra of ligands and their complexes, their coordination sites were proposed. The IR spectra of the Schiff bases had a broad absorption band at $3190-3210\text{ cm}^{-1}$ which was assigned to the enolisable OH group of the benzoylacetone and dibenzoylmethane moiety. These broad spectra indicated the presence of hydrogen bonds. These bands showed strengthened disappearance in the complexes in which enolic proton are completely displaced by the central tin metal. . The ligands showed no absorption at the range $(1670-1690)\text{ cm}^{-1}$, which indicated the absence of free carbonyl groups and thus indicating the enolic formation. The band at the range $(1601-1621)\text{ cm}^{-1}$ was assigned as the presence of azomethine group in the Schiff base ligands. In the organotin complexes, the azomethine group was shifted to lower frequency in the region $(1570-1611)\text{ cm}^{-1}$ that indicated the donation of lone pairs of nitrogen through the azomethine group that was confirmed by appearance of new bands at $434-457\text{ cm}^{-1}$ due to (Sn-N). The new bands at $550-562\text{ cm}^{-1}$ supported the presence of (Sn-O) that indicated coordination of oxygen to central tin metal. The band lying in the range $618-732\text{ cm}^{-1}$ indicated the presence of (Sn-C) supporting coordination of carbon to central tin atom.¹⁸⁻¹⁹

NMR spectroscopy

¹H NMR

On comparison of ¹H NMR of the ligands and their complexes, coordination of ONO has been proposed. The ¹H NMR spectra of the Schiff bases have a sharp singlet peak at $\delta 9.02-9.06$ and $\delta 10.03-10.05$ which is assigned to the enolisable OH group of the benzoylacetone and dibenzoylmethane moiety, which disappears on complexation confirms the participation of enolic hydrogen to the tin moiety. A sharp singlet appears in the range $\delta 12.33-12.36$ and $\delta 13.21-13.31$ is assigned for the phenolic OH group in schiff bases of benzoyl acetone and dibenzoylmethane respectively, which disappear in the complexes indicating the participation of phenolic hydrogen.²⁰⁻²¹ The sharp singlet in the range $\delta 5.60-6.08$ shows the vinylic hydrogen and the absence of signal near 3ppm for 2H indicate the absence of keto form and confirm enolic form. The deprotonation and coordination of enolic and phenolic hydrogen is confirmed by the absence of the signals in complexes. The methyl group appeared in the range $\delta 1.56-2.29$ with sharp singlet of 3H for ligands 1 and 2.

¹³C NMR

In the ¹³C NMR spectra of the ligands, the signal for C-OH enolic appeared at $\delta 185.83-188.62$ which show shift in the position of carbonyl oxygen in the range $\delta 176.84-179.71$ alongwith the deprotonation of enolic C-OH indicate the formation of complexes. The phenolic C-OH appeared at $\delta 142.04-150.08$ which shifted the position of oxygen in the range $\delta 155.79-157.85$ showing complexation through phenolic oxygen. The vinylic carbon of ligands show signal at $\delta 94.04-96.77$ which appeared downfield to $\delta 98.16-99.39$ in complexes. The aromatic carbon appeared in the range from $\delta 117.86$ to 136.89 in ligands and complexes. The azomethine carbon appeared in the range $\delta 163.05-165.58$ which shifted to downfield on complexation indicates involvement of nitrogen bonding to complexes. The methyl carbon appeared in the range $\delta 19.69-20.95$. In the complexes, phenyl group showed signal at $\delta 128.61$ for meta carbon, $\delta 130.22$ for para carbon, $\delta 135.11$ for ortho carbon, and $\delta 138.79$ for terminal carbon in Ph_2SnL_1 , the butyl group carbon signals appeared at $\delta 13.74, \delta 25.09, \delta 35.04, \delta 39.42$ in Bu_2SnL_1 .²²⁻²³

^{119}Sn NMR

The ^{119}Sn NMR chemical shifts of the Organotin complexes recorded in DMSO shown in table. A sharp singlet appeared in the spectra in the range from δ -125.24 to δ -166.72 for methyl complexes ($\text{Me}_2\text{SnL}_{1-2}$), from δ -180.23 to δ -198.41 for ethyl complexes ($\text{Et}_2\text{SnL}_{1-4}$), from δ -205.12 to δ -270.75 for butyl complexes ($\text{Bu}_2\text{SnL}_{1-2}$) and from δ -302.18 to δ -326.35 for phenyl complexes ($\text{Ph}_2\text{SnL}_{1-4}$). These sharp singlet chemical shifts revealed the formation of pentacoordinated tin centres in the complexes.²⁴⁻²⁵

X-RAY Powder Diffraction Analysis

From XRD powder diffraction analysis of the compounds, it was revealed that the compounds were crystalline in nature. A scan rate of about 2 min was applied to record the X-ray powder diffraction of the compounds over the range $2\theta = 10$ -80 degree and average crystallite size d_{XRD} was calculated to acquire impending regarding propulsive of the compounds. X-ray diffraction analysis of compounds exhibit the crystalline peak with maxima at $2\theta=27.4$, $d = 1.506 \text{ \AA}$, and $\text{FWHM}=60.016$ for compound (Ph_2SnL_1) shown in figure 1. Powder XRD of all the other compounds exhibited their crystalline nature. The particle size of the compounds was calculated by Debye-Scherrer formula and was found approximately 54 nm to 65 nm.

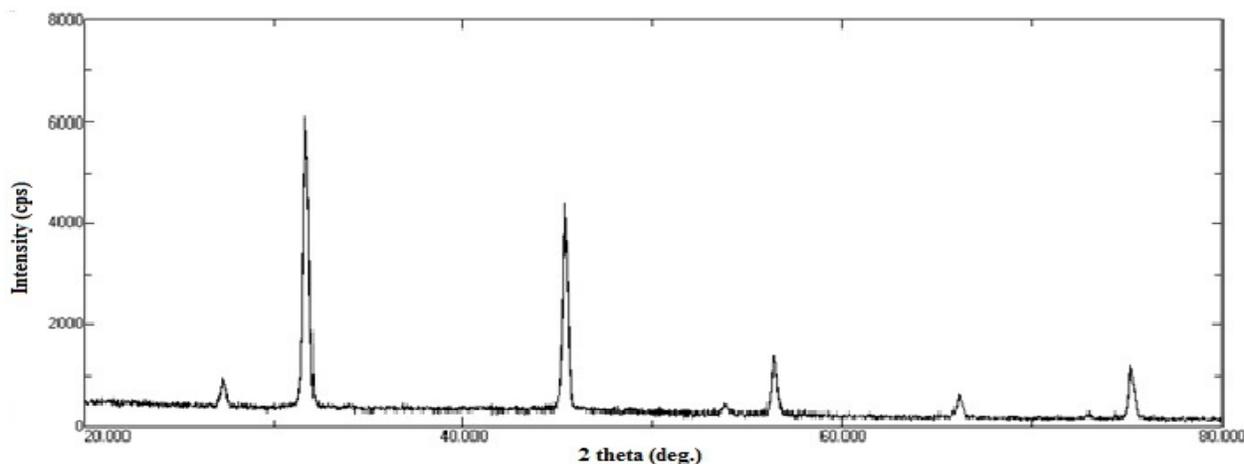


Figure 1. XRD Pattern in compound (Ph_2SnL_1)

Antimicrobial activities

Test microorganisms used

Gram positive bacteria *Bacillus cereus* (MTCC no.10072), *Staphylococcus aureus* (MTCC NICM no. 2901), gram negative bacteria *Escherichia coli* (MTCC no. 732), *pseudomonas aeruginosa* (MTCC 424) and fungi *Aspergillus niger* (MTCC no.7678), *Aspergillus flavus* (ITCC no.7680). All the bacteria were cultured on nutrient agar, whereas fungi were cultured on Potato dextrose broth (PDB) and ciprofloxacin was used as standard antibacterial drug and fluconazole was used as standard antifungal drug. Nutrient agar & Sabouraud dextrose agar were used as culture medium for bacteria and fungi respectively, and DMSO was used as solvent control for the biological activity.²⁶⁻²⁷

Determination of Biological assay

The serial dilution method was used for the evaluation of biological activities. The stock solution of all the compounds was prepared in dry DMSO with concentration 1mg/ml. The stock solution was added to

the nutrient broth to form first dilution (50µg/mL). Further the solution is diluted to 0.75µg/mL. The bacteria and the fungi were inoculated to each solution and then it was kept in incubator at 37°C for 24h in case of bacteria and for 7 days in case in fungi. Then, the MIC (minimum inhibitory concentration) was determined.^{22,24}

The antimicrobial data prompted the more activity of complexes than the ligands. This increased activity of the complexes might be the result of coordination with metal ion explained on basis of chelation theory. The complexes were more toxic towards Gram positive strains as compared to Gram negative strains which may be attributed to the fact that the cell walls of Gram negative strains have more antigenic properties due to the presence of an outer lipid membrane of lipopolysaccharides. Phenyl Complexes were found to be more active against the tested strains due to electron releasing ability of phenyl group that increase delocalization of π -electrons in chelate ring and lipophilicity of the complexes was enhanced as shown in table 1.

Table 1. Antimicrobial activities of Schiff base ligands and their Organotin complexes

Compound	MIC (µmol/ml)					
	<i>E.coli</i>	<i>P.Aeruginosa</i>	<i>B.ceres</i>	<i>S. aureus</i>	<i>A. niger</i>	<i>A. flavus</i>
H ₂ L ₁	0.046794	0.023397	0.046794	0.023397	0.01168	0.023397
H ₂ L ₂	0.024693	0.024693	0.049386	0.024693	0.012327	0.024693
Ph ₂ SnL ₁	0.011594	0.005788	0.005788	0.002894	0.002894	0.005788
Bu ₂ SnL ₁	0.012521	0.006251	0.006251	0.006511	0.003125	0.006251
Me ₂ SnL ₁	0.030116	0.007517	0.015058	0.015058	0.007517	0.007517
Et ₂ SnL ₁	0.028211	0.007041	0.014105	0.014105	0.007041	0.007041
Ph ₂ SnL ₂	0.011903	0.005942	0.005942	0.002971	0.002971	0.005942
Bu ₂ SnL ₂	0.014566	0.007271	0.007271	0.003636	0.003636	0.007271
Me ₂ SnL ₂	0.015584	0.00778	0.015584	0.008104	0.00778	0.00778
Et ₂ SnL ₂	0.012883	0.006431	0.012883	0.006699	0.006431	0.006431
Ciprofloxacin	0.004706	0.004706	0.004706	0.004706	-	-
Fluconazole	-	-	-	-	0.010187	0.010187

Conclusion

The synthesized complexes were prepared by reaction of β -diketones and aminophenols. NMR studies, IR studies, mass analysis, determined the characterized complexes. All the complexes showed biological potency. The phenyl complexes show more activity.

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